D.-W. Lee, Däniken/Switzerland

Ionizing rays make it possible to recycle PTFE waste

Valuable properties of PTFE – also referred to colloquially as Teflon – are produced by its high binding energy (C-F: 507 kJ/mol), the high degree of crystallinity (50 to 95%) and the extremely high molecular weight (500 000 to 1 million). This provides the basis for the outstanding thermal, chemical, mechanical and electrical properties. Worldwide production is approximately 55 000 t/a. In Western Europe approximately 11 000 t/a is used in the chemical, automobile, mechanical and electrical industries and medical and domestic appliances [1].

PTFE recycling problematic

Recycling PTFE waste has become particularly important in production and processing for economic and toxicological reasons:

- At the beginning and the end of the process large faulty quantities accumulate from each polymerization batch until the optimal production conditions have been reached. These can amount to 20 to 30%.
- Depending on the complexity, up to 30% waste is produced during further machining to form compacts,.
- In addition, this waste is much more difficult to dispose of due to its excellent chemical stability. Moreover, toxic substances such as fluoric acid, fluorophosgene, fluoroalkane, perfluoroisobutene, are produced during combustion [2].

The approach: degradation to powder

PTFE has many fields of application due to its extraordinarily good properties in high-molecular form as well as in low-molecular form. Recycling is therefore based mainly on a degradation process. Different valuable materials are thereby produced depending on the degradation process:

- Perfluoric acid derivates (degradation in oxygen atmosphere) [3],
- Perfluoroalkenes or perfluoroalkanes (degradation in inert gas atmosphere),

- Pure or modified PTFE fine powder (degradation in air or modified atmospheres).

The fine powder is produced by subsequent milling and is used on an industrial scale because of its versatile uses and easy production. This is a relatively low-molecular product with a relative molar mass of 30 000 to 500 000 (crystallite melting point 320 to 326°C, melting viscosity at approx. 102 Pa · s). A material degraded to such a great extent is also referred to as a wax. The degradation requires an energy supply. This can be inserted via thermal or ionizing radiation.

With thermal degradation, a brittle, low-molecular PTFE wax is produced. Approximately 60 to 70% of the PTFE waste used is recovered as wax. The rest is lost in gaseous depolymerization products, e.g., as tetrafluoroethylene, hexafluoropropylene, octafluorocyclobutane, fluorophosgene, perfluoroisobutylene, which are very toxic [4, 5].

The way: ionizing irradiation

A comparably simple and safe way of degrading PTFE is the use of ionizing radiation. This degrades the PTFE macromolecule immediately. In the presence of atmospheric oxygen, in addition to the chain splitting, oxidation reactions occur, wherein a much smaller radiation dose is necessary for changing the PTFE properties. The degradative reactions occur mainly in the amorphous phases [6]. The molecular weight and amorphous constituents are thereby reduced, but the crystallinity is increased. These degradative reactions can be followed based on the melt flow index measurement (Fig. 1).

Fig. 1 Change of the melt flow index of PTFE after irradiation (DIN 53735: 380°C/ 3.8 kg)

With a dosage of approximately 200 kGy, pourable low-molecular PTFE is produced from hardly pourable high-molecular PTFE. With approximately 300 kGy, an average relative molar mass of 50 000 to 400 000 results, wherein the brittleness of the material increases. Table 1 shows how strength and breaking elongation decrease with a low radiation dose of 100 kGy [7].

Table 1 Mechanical strength and breaking elongation of irradiated PTFE film

Sample	Dose kGy	Strength N/mm^2	Breaking elongation %
Unirradiated	0	26.9	129 (+ 30)
Irradiated in vacuum	100	13.6	10 (+ 2)
Irradiated in air	100	0	0

Fig. 2 PTFE waste in a polyester vessel (A) and aluminum vessel (B)

Irradiation therefore on the one hand facilitates milling, and on the other hand the material becomes pourable and free-flowing. The high penetration capacity of gamma rays [8, 9] provides a high degree of effectiveness. Although the low dosage rate of gamma rays could have disadvantages due to the long irradiation period necessary, this is accepted because of the advantageous oxidative degradation.

When is the treatment worthwhile?

Costs of up to DM 9/kg can be incurred (1991), depending on the expenditure of the recycling and the cleanness of the secondary material,. The collected PTFE waste can be roughly divided into four categories:

- Lumpy and not free-flowing faulty batches of the polymerization,
- Filled material,
- Low-oriented material, e.g., waste from tape production,
- Highly oriented material, e.g., waste from compact production from rods or hoses.

Category 1 as the most expensive is an unsintered and easily coagulable dried dispersion in powder form, which becomes pourable and free-flowing through irradiation. The particle size is reduced to approximately 1 μm by mixing with high shear.

Category 2 waste, which is filled with glass fibers, bronze or molybdenum sulfide, makes recycling problematic. Glass fiber filled PTFE waste becomes dark-colored through irradiation (the glass fibers become discolored due to the irradiation). This coloration reduces the quality level. Bronze filled PTFE waste is not attractive due to the particle size of the bronze particles of approximately 40 μm, because fine milling would be much

too expensive. However, it is available free of charge and is not currently being utilized. However, as the total amount of recyclable waste becomes scarce, it is to be expected that efficient utilization methods will likewise be developed for waste of this type.

Waste of categories 3 and 4 is often dirty. This dirt can be removed by washing with acid solution (e.g., sulfuric acid, nitric acid or perchloric acid).

Fig. 3 Loading PTFE waste in carriers for treatment with gamma rays

Table 2: List of the plastics that are processed with PTFE fine powder

Thermoplastics	Cross-linked plastics
Polyacetal	Epoxide masses
Polycarbonate	Aminoplastic resins
Polyamide	Phenolic resins
Polyimide	UP resins
Polysulfone	Polyurethane
Polyphenylene sulfide	Ethylene-propylene rubber
Polystyrene	Silicone rubber
Polypropylene	Styrene-butadiene rubber
Styrene-acrylonitrile copolymer	

The technical process

PTFE waste provided for recycling is packed in polyethylene bags, and these are then deposited in polyester vessels or aluminum vessels for irradiation (Fig. 2). If there is no gas outlet device, small amounts of sodium carbonate or calcium carbonate added in textile bags neutralize the toxic gases, such as HF, produced thereby.

These vessels are loaded in pallets in carriers (Fig. 3) and subsequently irradiated. Depending on the type of waste, e.g., powder, chips or rods, it is irradiated with 200 to 400 kGy. This irradiated brittle material is first pre-milled with the cutting mill and

subsequently milled with the turbo mill to form a fine powder with an average particle size of 10 to 200 μm.

Use of PTFE fine powder

The finely milled PTFE powder has properties similar to the original PTFE, such as good temperature resistance and good slip behavior, nonstick behavior, abrasion characteristics and friction behavior. Furthermore, this powder is easily pourable and can be mixed well homogenously with other plastics.

Approximately 700 t/a PTFE fine powder is produced in Western Europe. Due to its referenced properties it is used as an additive as follows:

Additive in plastic compacts

PTFE fine powder reduces wear by friction and stick-slip tendency in compacts (Table 2) with increased fire resistance. With abrasive stress, PTFE fine powders migrate out of the base material and form an oil film on the surface of the rubbing partner. PTFE fine powder has advantages in the case of reinforced plastics, because, e.g., the glass fibers close to the surface are embedded therein and are thus protected from wear. For optimum wear behavior, approximately 20% PTFE fine powder is used in the case of partially crystalline plastics, and approximately 15% is used with amorphous plastics and elastomers.

Additive for printing inks:

In offset printing inks and gravure printing inks PTFE fine powders as an additive improve the slip and sliding properties, surface smoothness and shine and scrub resistance. This has special advantages with fast running printing machines.

Additive in lacquers

PTFE fine powder is used for the purpose of surface finishing in lacquers for technical and domestic appliances, in anti-corrosion lacquers or special water-repellant lacquers, likewise in coil coating of metal tapes.

Additive in oils and greases:

PTFE fine powders are used, e.g., in lubricating oils for high-speed machine parts such as motors, gears, pumps, kneading machines, etc. High temperature-resistant greases for aerospace are produced by incorporating PTFE fine powder in silicon oil.

Solid lubricant:

White PTFE fine powder is suitable for the solid lubricant effect, e.g., with looms in the textile industry, where grease and lubricant spots must be avoided.